41004-049-30 CONT

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C03C 17/36, 17/34 — A1

(11) International Publication Number: **WO 00/29346**

(43) International Publication Date: 25 May 2000 (25.05.00)

(21) International Application Number: PCT/EP99/08691

(22) International Filing Date: 5 November 1999 (05.11.99)

(30) Priority Data:
98 203 749.1 6 November 1998 (06.11.98) EP

(71) Applicant *(for all designated States except US)*: GLAVERBEL [BE/BE]; Chaussée de la Hulpe, 166, B–1170 Brussels (Watermael–Boitsfort) (BE).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: DEGAND, Etienne [BE/BE]; Centre R. & D., Rue de l'Aurore, 2, B–6040 Jumet (BE).

(74) Agents: VANDENBERGHEN, Lucienne et al.; Glaverbel, Department Intellectual Property, Centre R. & D., Rue de l'Aurore 2, B–6040 Jumet (BE).

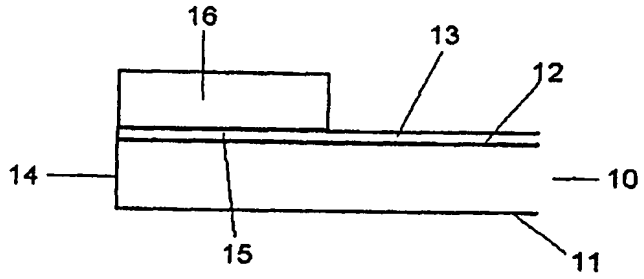
(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: GLAZING PANELS



(57) Abstract

A method of manufacturing a glazing panel comprises the steps of: a) taking a glazing panel having on one of its surfaces (i) a substantially transparent coating layer having a transformable portion, and (ii) an enamel material associated with the transformable portion of the coating layer; and b) causing an interaction between the tranformable portion of the coating layer and the enamel material associated therewith by heating the glazing panel to a temperature above about 300 °C. This may render a portion of the coating layer less susceptible to corrosion and/or non–conductive to electricity.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

Glazing panels

This invention relates to glazing panels and particularly but not exclusively to automotive glazing panels provided with coating layers.

One or more coating layers may be applied to a glazing panel to enhance its performance, for example, to render the panel electrically heatable, to provide solar control or to reduce reflection. Such coating layers may comprise a single coating film or a stack of coating films.

In some instances, it is not desirable for the entire glazing panel to be covered with the coating layer. If the coating layer is to be electrically heated, for example to de-mist the rear screen of a car window, it may be desirable for the perimeter of the rear screen to be electrically isolated. Alternatively, if the coating layer is a solar control coating sandwiched between two panes of glass of a laminated car windscreen it may be desirable for the perimeter to be rendered insusceptible to corrosion which could otherwise cause undesirable coloured spots or stains (notably where the coating layer comprises one or more layers of silver).

It has previously been proposed to mechanically remove a coating layer around the periphery of a glazing panel, for example by abrasion, or to mask the periphery of the glazing panel prior to depositing the coating. Chemical removal of portions of a coating layer, in particular by acid attack, are also known. Nevertheless, these methods all present certain disadvantages, notably in terms of the aesthetic result produced and the difficulties of being practised on an industrial scale.

According to one aspect, the present invention provides a method as defined in Claim 1.

The coating layer may be electrically conductive. The coating layer may cover substantially an entire surface of the glazing panel or substantially the entire central portion of a surface of the glazing panel.

The interaction between the transformable portion of the coating layer and the band of an enamel material associated therewith preferably changes the properties of the transformable portion of the coating layer. For example:

- where the coating layer is electrically conductive, the interaction may render the transformable portion of the coating layer non-conductive, preferably without rendering other portions of the coating layer non-conductive; and/or
- the interaction may render the transformable portion of the coating layer less susceptible to corrosion.

The interaction may cause chemical changes to the transformable portion of the coating layer and may result from diffusion between the transformable portion of the coating layer and the band of an enamel material associated

therewith. In this latter case, the transformable portion of the coating layer may be substantially absorbed into the band of an enamel material associated therewith so that only the enamel material is visible with the naked eye through the glazing panel.

The interaction may be caused by heating the glazing panel to a temperature above about 300° C, 350° C, 375° C, 400° C, 425° C, 450° C, 475° C, 500° C, 525° C, 550° C, 575° C, 600° C, 625° C, 650° C, 675° C or 700° C. It may not be essential for the entire glazing panel to be reach such a temperature but merely the portion at which the interaction is intended to occur.

The heating of the glazing panel may cause local destruction, break down or disintegration of the transformable portion of the coating layer. Where the enamel is a black or dark coloured enamel, this may occur due to the enamel material associated with the transformable portion of the coating layer causing local "overheating" of the transformable portion of the coating layer.

Clearly, there may be more than one transformable portion of the coating layer, each transformable portion having an enamel material associated therewith.

Where the coating is substantially electrically conductive it may have a resistance of less than 30 ohms per square. Preferably, such a coating has a resistance of less than 20, 15 or 10 ohms per square; such resistances may be achieved with pyrolytic coatings based on, for example, doped tin oxide. Even more preferably, such a coating has an electrical resistance of less than 6, 5, 4, 3 or 2 ohms per square; such resistances may be achieved with sputtered coatings having one or more spaced silver containing layers.

The enamel material is preferably positioned over the transformable portion of the coating layer. This allows the coating layer to be deposited over the entire surface of a large sheet of glass, for the sheet of glass to be subsequently cut to the desired dimensions of the glazing panel and for the enamel material to then be deposited over the coating layer. This greatly facilitates production, notably because it avoids the difficulties and associated expense of applying a coating layer to glazing panels which have already been cut to their desired size.

Alternatively, the coating layer may be deposited over an enamel material which has previously been deposited on the glazing panel.

The enamel material may serve one, and preferably a combination of the following functions: It may:

- reduce susceptibility of the coating layer (and particularly the edge of the coating layer) to corrosion and/or

- provide an aesthetic masking band, for example to hide the fixation of the glazing panel to a supporting structure and/or
- electrically isolate a portion of an electrically conductive coating layer and/or
- mask vision through a portion the glazing panel and/or
- wholly or partially mask an electrical connector associated with an electrically conductive coating layer.

The invention may be advantageously used where the coating layer extends to the periphery of the glazing panel and the enamel material forms an opaque band around the periphery.

The coating layer may be a solar control filter, an electrically conductive film, a low emissivity filter or some other type of coating; it may be deposited by sputtering, by pyrolysis from one or more liquid precursors, by pyrolysis using chemical vapour deposition or in any other suitable way.

The enamel material associated with the transformable portion of the coating layer may comprise silver. This is believed to facilitate interaction with a coating layer which comprises one or more silver layers.

According to further aspects, the present invention provides for use of a method as defined in claim 10, an automotive vehicle glazing as defined in claim 11 and a glazing panel as defined in claim 12.

Examples of the present invention will now be described, by way of example only, with reference to the accompanying drawings of which:

Fig 1 is a plan view of a glazing panel which forms part of a car windscreen;

Fig 2 is a section of an edge portion of the glazing panel of Fig 1 prior to heating;

Fig 3 is a section of an edge portion of the glazing panel of Fig 1 after heating;

Fig 4 is a simplified section similar to Fig 2 showing a further embodiment.

To facilitate clarity, the thicknesses of the layers shown in the figures have not been drawn to scale.

According to one example, the invention is performed using a glass glazing panel 10 intended to form one sheet of a laminated car windscreen. By convention the faces of a glazing panel are counted from the exterior of the structure (position 1) to the interior. Position 2 of a monolithic structure is thus the interior

face (i.e. facing towards the inside of the vehicle or building to which it is attached) whilst for a laminated structure position 2 is the interior face of the external sheet (which contacts the laminating pvb layer, for example in current windscreens)).

The glazing panel 10 carries a coating layer 13 in position 2 which extends to the edges 14 of the glazing panel. The coating layer is an electrically heatable, solar control coating deposited by magnetron sputtering and consists of the following layers: ZnO antireflective layer/ Ti barrier/ Ag infra red reflecting layer/ Ti barrier / ZnO antireflective layer/ Ti barrier/ Ag infra red reflecting layer/ Ti barrier / ZnO antireflective layer. Coating layers of this type are well known in the art and the present invention is not limited to this particular type of coating layer. The invention is particularly effective for use with vacuum coated layers, for example sputtered layers, which are not generally mechanically resistant . Nevertheless, it may also be beneficial when applied to "hard" coating layers, for example, those formed pyrolitically. It is especially useful with coating layers which are heat treatable by, for example bending and/or tempering, and can thus be applied to a flat sheet of glass which is subsequently shaped and or heat treated.

As shown in Fig 2, the coating layer 13 has a transformable portion 15 which in this case forms a band around the entire periphery of the glazing panel. A band of enamel 16 is associated with the transformable portion 15 of the coating layer, in this case being silk screen printed over the coating layer 13. In this example, the transformable portion 15 of the coating layer is situated directly below and in direct contact with the enamel material 16 though this need not always be the case.

Good results may be obtained using the enamel 1T55M056 supplied by Johnson-Matthey which, after firing has the following components:

Si	15.5	Y	
Bi	42.2	Hf	
		S	0.0925
Al	0.142	Cl	0.0416
Mn	0.145	Pb	
Mg	0.138		
Ca	0.284		
Na	0.843		
K	0.367		
Ti	2.95		
P	0.0226		
Fe	0.134		
Mo			
Co			
Cr	20.5		
Cu	12.9		
Ag	2.33		
Ni	0.0363		
Zr			
B	1.82		
Ba			
Sr			

The principle components of this enamel are (Bi4(SiO4)3) and (Bi4Ti3O12). When applied to the glazing panel prior to firing the enamel also contains solvents, for example, polyvinylpyrrolidone (PVP) and xylene; these evaporate when the enamel is heated.

When this particular enamel is used in position 2 of a laminated structure it is preferred to carry out a heating process with the enamel exposed to the atmosphere. This may provide a "pre-firing" or evaporation process which can reduce the risk of blisters forming in the enamel in position 2 if the glazing panel is subsequently heated with a sheet of glass overlying the enamel due to evaporated gasses from the enamel being trapped. In this example, the glazing panel is initially raised to a temperature of about 450 °C with the enamel material exposed to the atmosphere.

The glazing panel was then assembled with another sheet of glass, the other sheet of glass lying in contact with the face at position 2 of the glazing panel, and subjected to a bending and tempering process reaching a temperature of about 650 ° C in preparation for the glazing panel and the other sheet of glass to be laminated together using a sheet of pvb to form a windscreen.

Heating of the glazing panel caused an interaction between the band of enamel 16 and the transformable portion 15 of the coating layer.

If an enamel suitable for firing in position 2 is used, the heating operation may be carried out as part of a bending and/or tempering operation. Particularly in cases where the glazing panel does not require bending simultaneously with an associated sheet of glass, the heating of the present invention is preferably carried out during a bending and/or tempering and/or heat treatment process. This is particularly the case for monolithic glazings, for example, rear windows, side windows and sunroofs for vehicles.

In the present case, the transformation renders the transformable portion 15 of the coating layer non-conductive to electricity and reduces its susceptibility to corrosion. As the transformation portion forms a band around the edge of the glazing panel this may not only prevent corrosion at the edge of the glazing but also provide an effective barrier which prevents corrosion of the rest of the coating layer.

As shown in Fig 3, after the heat treatment, only the enamel band is visible through the glazing panel and it is not visually perceivable with the naked eye that the enamel band and the transformable portion 15 of the coating layer were originally superimposed.

The structure of the enamel material may be altered by the heating step and solvents initially present in the enamel material may evaporate. Nevertheless, once the enamel material has been applied to the glazing panel it is not removed but is incorporated in the finished glazing panel. This avoids the need for a washing or removing operation which is commonly required with acid attack techniques for removing coating films.

In Fig 4, the enamel band also masks an electrical connector 21 and a portion of a silver containing frit 20 intended for providing electrical power for heating the coating layer.

The invention may be used with a wide variety of glazing panels, for example, vehicle windscreens, vehicle rear windows, vehicle sunroofs, vehicle side windows and architectural glazing panels.

The utility of the invention is not limited to any particular mechanism of interaction between the transformable portion of the coating layer and the enamel material. Nevertheless, when the coating layer contains at least one layer of silver it is thought that one mechanism which causes transformation of the transformable portion of the coating layer may be agglomeration or conglomeration of the silver of the coating layer so that the silver forms into discontinuous pools. This may then be

incorporated into the structure of the enamel. This may be detectable by examining the concentration of silver at the surface of the enamel material after the interaction, particularly if the coating layer was originally deposited over the enamel layer.

Claims

1. A method of manufacturing a glazing panel comprising the steps of:
a) taking a glazing panel having on one of its surfaces
(i) a substantially transparent coating layer having a transformable portion, and
(ii) an enamel material associated with the transformable portion of the coating layer; and
b) causing an interaction between the transformable portion of the coating layer and the enamel material associated therewith by heating the glazing panel to a temperature above about 300° C.

2. A method in accordance with Claim 1, in which prior to heating of the glazing panel the enamel material is positioned over the transformable portion of the coating layer .

3. A method in accordance with Claim 2 or Claim 3, in which the coating layer extends substantially to at least one peripheral edge of the glazing panel and the enamel material is deposited over at least one portion of the coating layer positioned at that peripheral edge.

4. A method in accordance with any preceding claim , in which the coating layer is sputter deposited and comprises at least one layer of an infra red reflecting material sandwiched between antireflective dielectric layers.

5. A method in accordance with any preceding claim, in which the coating layer comprises a pyrolytically deposited layer.

6. A method in accordance with any preceding claim in which heating of the glazing panel causes substantial destruction of the transformable portion of the coating layer.

7. A method in accordance with any preceding claim, in which the transformable portion of the coating layer is rendered substantially non-conductive to electricity.

8. A method in accordance with any preceding claim, in which visual inspection of the glazing panel does not reveal that the enamel material deposited over transformable portion of the coating layer was so deposited rather than being deposited in the absence of the coating layer.

9. A method in accordance with any preceding claim comprising the further step of:

c) arranging an electrical connector which is electrically connected to the coating layer at least partially over the enamel material.

10. Use of a method in accordance with any preceding claim to reduce edge corrosion of the coating layer.

11. An automotive vehicle windscreen, rear window, side window or sunroof comprising a glazing panel manufactured according to any preceding claim.

12. A glazing panel comprising a glass substrate, a substantially transparent electrically conductive coating layer supported on the glass substrate and at least one band of enamel material characterised in that the at least one band of enamel material comprises traces of the electrically conductive coating layer resulting from an interaction between the at least one band of enamel material and the coating layer such that the at least one band of enamel material provides a discontinuity in the electrical conductivity of the coating layer.

13. A glazing panel in accordance with claim 12, in which the electrically conducting coating layer is a sputtered, solar control coating comprising at least one layer of silver or silver alloy.

Fig 1

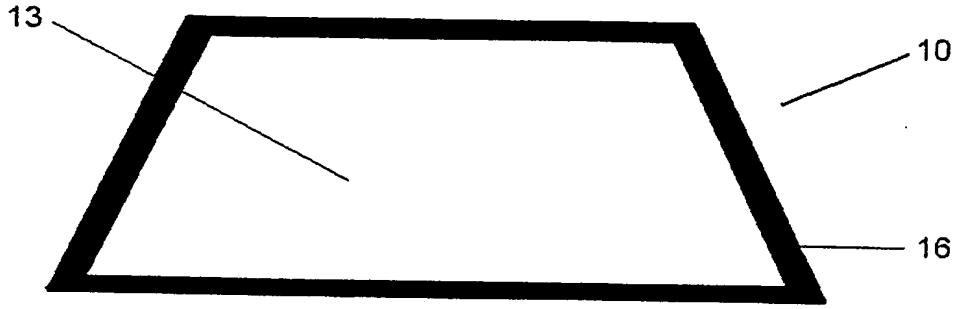


Fig 2

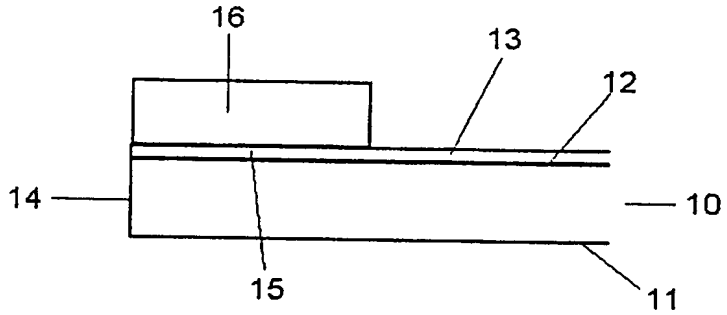


Fig 3

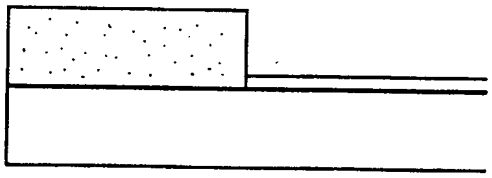
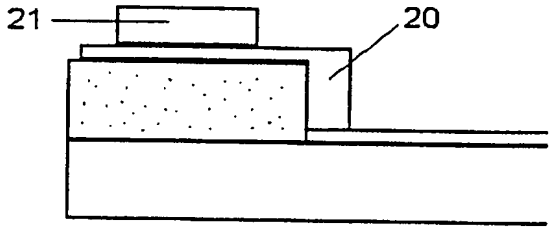


Fig 4



INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/EP 99/08691

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C17/36 C03C17/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 546 365 A (DEGUSSA AKTIENGESELLSCHAFT) 16 June 1993 (1993-06-16) claims 1-5,8; figure	1,2, 10-13
A	EP 0 226 901 A (LEYBOLD HERAEUS GMBH) 1 July 1987 (1987-07-01) claims 1,6; figure 2	1-13
A	EP 0 084 262 A (FORD MOTOR COMPANY LIMITED) 27 July 1983 (1983-07-27) abstract	3
A	DE 10 88 198 B (LIBBEY OWENS FORD GLASS COMPANY) column 4, line 59 -column 5, line 26	1,2, 10-13

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 April 2000	12/04/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Reedijk, A

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

information on patent family members

Inter nal Application No
PCT/EP 99/08691

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 546365	A	16-06-1993	FR	2684665 A	11-06-1993
			DE	59202612 D	27-07-1995
			ES	2073846 T	16-08-1995
			JP	2978021 B	15-11-1999
			JP	5238780 A	17-09-1993
			US	5300349 A	05-04-1994
EP 226901	A	01-07-1987	DE	3543694 A	19-06-1987
			JP	62216945 A	24-09-1987
			US	5011745 A	30-04-1991
			US	4830876 A	16-05-1989
EP 84262	A	27-07-1983	US	4407847 A	04-10-1983
			CA	1187039 A	14-05-1985
			JP	58115040 A	08-07-1983
DE 1088198	B		NONE		